SOLUBILITY AND CATION EXCHANGE PROPERTIES OF SYNTHETIC HYDROXYAPATITE AND CLINOPTILOLITE MIXTURES

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ABSTRACT

A zeoponic plant growth system is defined as the cultivation of plants in artificial soils, which have zeolites as a major component. These systems: 1) can serve as a controllable and renewable fertilization system to provide plant growth nutrients; 2) can mitigate the adverse effects of contamination due to leaching of highly soluble and concentrated fertilizers; and 3) are being considered as substrates for plant growth in regenerative life-support systems for long-duration space missions. Batch-equilibrium studies of the dissolution and ion-exchange properties of mixtures of naturally-occurring Wyoming clinoptilolite (a zeolite) exchanged with K^+ or NH_4^+ and synthetic hydroxyapatite were conducted to determine: 1) the plant-availability of the macro-nutrients NH_4-N, P, K, Ca, and Mg and 2) the effects of varying the clinoptilolite to hydroxyapatite ratio and the ratio of exchangeable cations (K^+ vs. NH_4^+) on clinoptilolite extraframework sites. The nutrients NH_4-N (19.7 to 73.6 mg L^{-1}), P (0.57 to 14.99 mg L^{-1}), K (14.8 to 104.9 mg L^{-1}), and Mg (0.11 to 6.68mg L^{-1}) are available to plants at sufficient levels. Solution Ca concentrations (0.47 to 3.40 mg L^{-1}) are less than optimal. Solution concentrations of NH_4^+, K^+, Ca^{2+}, and Mg^{2+} all decreased with increasing clinoptilolite to hydroxyapatite ratio in the sample. Solution concentrations of phosphorous initially increased, reached a maximum value and then decreased with increasing clinoptilolite to hydroxyapatite ratio in the sample. The NH_4^+-exchanged clinoptilolite is more efficient in dissolving synthetic hydroxyapatite than the K^+-exchanged

clinoptilolite. This suggests that NH_4^+, which is less selective at clinoptilolite extraframework sites than K^+, is exchanged more readily by Ca^{2+} and thereby enhances the dissolution of the synthetic hydroxyapatite.

KEYWORDS

bioregenerative life support, clinoptilolite, hydroxyapatite, zeolite, zeoponics
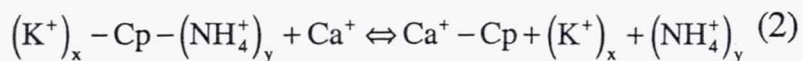
INTRODUCTION

An artificial plant growth substrate composed of zeolite and phosphate minerals (i.e. zeoponic substrate) can serve as a controllable and renewable fertilization system to provide plant growth nutrients [1-4]. Moreover, the slow release nature of zeoponic substrates can mitigate the adverse effects of ground- and surface-water contamination due to leaching of highly soluble and concentrated fertilizers. Zeoponic substrates have been developed at the National Aeronautics and Space Administration (NASA) as plant growth substrates for use in bioregenerative life-support systems required for future long-duration space missions (e.g., Mars transit vehicles, planetary outposts). These zeoponic systems slowly release some [5] or all of the essential plant growth nutrients [6]. They consist of NH_4^+- and K^+-exchanged clinoptilolite-rich tuff (Cp, chosen due to its high selectivity for NH_4^+ and K^+) and either natural or synthetic hydroxyapatite (Ap). The concept behind this zeoponic system is that the low solubility exhibited by Ap will be overcome by the

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sequestering of Ca^{2+} through ion-exchange by the Cp. Specifically the chemical equilibria among Cp, Ap, and water will be dominated by the dissolution of Ap, which releases Ca into solution, and subsequent ion exchange between Ca^{2+} and K^+ or NH_4^+ on extraframework sites in the Cp. According to Allen et al. [5] these reactions can be represented as:

$$Ca_5(PO_4)_3OH + 3H_2O \Leftrightarrow 5Ca^{2+} + 3HPO_4^{2-} + 4OH^- \quad (1)$$

and

$$(K^+)_x - Cp - (NH_4^+)_y + Ca^+ \Leftrightarrow Ca^+ - Cp + (K^+)_x + (NH_4^+)_y \quad (2)$$

where x,y = 2,0; 1,1; or 0,2.

Reaction (1) represents a simplified dissolution of Ap ignoring the trace micronutrients present. Reaction (2) represents the exchange of Ca^{2+} (which has dissolved into solution from Ap) by Cp that results in the shifting of both reactions to the right. The goals of this study are to, by means of a series of batch-equilibration experiments, determine: 1) the solution concentrations of the macro-nutrients NH_4-N, P, K, Ca, and Mg in synthetic Ap and Cp mixtures, 2) the solution concentration effects of varying the Cp to synthetic Ap ratio in these mixtures and 3) the solution concentration effects of varying the fraction of K^+ vs. NH_4^+ on extraframework sites of the Cp in these mixtures.

PREVIOUS WORK

Zeoponic systems have been successfully demonstrated in Cuba and Bulgaria, but these systems require periodic treatments with fertilizers or nutrient solutions (e.g. [7]). Moller and Mogensen [8] demonstrated an increase in soil solution P concentrations due to enhanced phosphate dissolution by the addition of Na-saturated synthetic zeolite. Lai and Eberl [9], Chesworth et al. [10], and Barbarick et al. [11] reported an increase in P released from phosphate rock by the addition of Cp. Allen et al. [5] performed batch-equilibrium experiments to determine the solubility and ion-exchange properties between Cp (from the San Miguel mine in Texas) and Ap-dominant phosphate rock from deposits in North Carolina and Tennessee. They concluded that the mixing of NH_4^+- and K-exchanged Cp with phosphate rock, increased the solubility of the phosphate rock and resulted in the simultaneous release of NH_4^+ and K^+ into solution. These mixtures provide enough N, P, and K in solution to support plant growth. Calcium in solution was lower than optimal for plant growth due to the removal of Ca^{2+} from solution by exchange onto extraframework sites in the Cp. The approach of this study is similar to Allen et al. [5] however a synthetic hydroxyapatite developed by Golden and Ming [12] was used in this study instead of natural apatite-rich phosphate rock materials.

MATERIALS

The starting materials consist of Cp mined from the Fort LeClede deposit of the Green River Formation in Sweetwater County, Wyoming [13] and a synthetic hydroxyapatite developed at NASA's Johnson Space Center Advanced Life Support Laboratory [12]. All materials were sieved and the 0.5 to 1.0 mm sieve

fraction was used for batch experiments. The compositions of the starting materials are shown in Table 1. Based on 72 oxygen per formula unit, the Cp has the formula $(Na_{3.55} K_{0.87} Ca_{0.63} Mg_{0.11} Fe_{0.03} Ti_{0.01} Al_{0.21}) Al_6 (Al_{0.66} Si_{3.34}) Si_{26} O_{72} \cdot 24 H_2O$. The Si to Al ratio is 4.27 which is greater than the Cp/heulandite boundary of 4.0 [14-15]. Sodium is the dominant extraframework cation with subsidiary amounts of K and Ca and trace amounts of Mg, Fe, and Ti. The Cp has a cation exchange capacity (CEC) of 199 $cmol_c$ kg^{-1} [16], which was determined by a CsCl method described by Ming and Dixon [17]. The Cp was exchanged into K^+- or NH_4^+- exchanged Cp using the method of Allen et al. [5]. The nutrient substituted synthetic Ap (Table 1) was synthesized using the method of Golden and Ming [12]. In addition to the major components Ca and P, it contains the plant nutrients K, Mg, S, Cu, Fe, Mn, Zn, Mo, B, and Cl.

EXPERIMENTAL METHODS

Sample Assembly

A series of batch-equilibration experiments were performed in which 100 mL of de-ionized water were combined with varying amounts of K^+-exchanged Cp, NH_4^+-exchanged Cp, and synthetic Ap in a 125 mL Erlenmeyer flask. Cp to synthetic Ap weight ratios of 1, 2, 4, 8, 16, and 32 were studied for ratios of K^+ to $NH_4^+ + K^+$ on Cp extraframework sites (E_K) of 1, 0.5, and 0. The 0.5 E_K value was achieved by combining equal parts of K^+-exchanged Cp and NH_4^+-exchanged Cp. For example, a sample with a Cp/Ap ratio of 4:1 and an E_K of 0.5 consisted of 1.000 g of K^+-exchanged Cp, 1.000 g of NH_4^+-exchanged Cp, and 0.500 g of synthetic Ap. In each

case the total solid was 2.5 g resulting in a constant fluid-solid ratio of 40 mL/g. Each flask was capped with a foam stopper to obtain free exchange with atmospheric CO_2 and was placed on an orbital shaker set at 90 rpm and 25° C. Each treatment was replicated three times.

Equilibration Time

The shaking time required for a mixture of Cp and Ap to approach a steady state has been studied by Allen et al. [5] and Beiersdorfer [18]. Allen et al. [5] recommended a shaking time of 96 hours based on measurement of solution K concentrations in mixtures of 0.25 g of Cp, 0.05 g of naturally occurring phosphate rock, and 10 mL of water in a stoppered centrifuge tube. Solution K concentrations increased rapidly for the first 16 hours of shaking followed by slight increases for up to 96 hours. There was little increase in K concentration between 72 and 96 hours. Beiersdorfer [18] measured concentrations of P and K as a function of shaking time in zeoponic substrates consisting of 2 g of K^+-exchanged Cp, 0.5 g of synthetic Ap, and 100 mL of de-ionized water in a 125 mL Erlenmeyer flask. Phosphorus and K concentrations increased rapidly over the first 210 hours and reached "steady state" concentrations after 400 hours of shaking time. Without explaining their selections, Lai and Eberl [9] and Barbarick et al. [11] selected 48 hours and Chesworth et al. [10] chose 70 hours for equilibration experiments containing zeolite and phosphate rock. Woods and Gunter [19] found no change in solution concentration in Na^+- and Cs^+-exchanged Cp-rich rock after 24 hours. Palmer and Gunter [20] found that near steady-state conditions were reached after 240 hours in Sr^{2+}-exchanged Cp. In

order to be confident that mixing time was adequate for achieving a steady state in solution concentrations, samples in this study were removed at 500 hours.

Analysis of Solutions

The supernatant solutions were filtered through a #42 Whatman filter (nominal (98% retention) pore size rating of 2.5 μm). Potassium, Mg, and Ca concentrations in solution were determined by flame atomic absorption spectroscopy. Phosphorous was determined using an ascorbic-acid, molybdophosphate-blue colorimetric method [21]. Ammonium, pH, and electrical conductivity were measured using ion selective electrodes. Ionic strength was calculated from measured electrical conductivity measurements using the empirical relationship of Griffin and Jurinak [22] where:

Ionic Strength (moles/liter) = 0.0127 Electrical Conductivity (decisiemens/meter). Least squares regression of data was performed using the software program DeltaGraph Pro version 3.0 (SPSS Inc. Chicago, IL).

This experimental procedure differs from Allen et al. [5] in that they placed mixtures containing 0.25 g of K^+-exchanged Cp and varying amounts of phosphate rock (to give the desired Cp/phosphate rock mass ratio) in stoppered centrifuge tubes containing 10 mL of deionized water. In these experiments we placed a total solid of 2.5 grams in 100 mL deionized water in order to hold the fluid to solid ratio constant (40 mL/g) for each treatment. The fluid to solid ratio was also held constant in the experiments performed by Lai and Eberl [9] (41.7 mL/g), Chesworth et al.

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[10] (50 mL/g) and Barbarick et al. [11] (2 mL/g). In the experiments of Allen et al. [5] the fluid to solid ratio was different (ranging from 20 to 38.1 mL/g) for each Cp to phosphate rock ratio studied.

RESULTS AND DISCUSSION

Solution pH, ionic strength, and P, NH_4, K, Mg, and Ca concentrations after 500 hours of shaking time for samples containing various Cp to synthetic Ap ratios, as well as varying E_K are shown in Table 2. Ammonium was not analyzed in samples that contained no NH_4^+-exchanged Cp (i.e. samples with E_K of 1). Potassium however, was measured at very low levels in solution in samples that contain only NH_4^+-exchanged Cp (i.e. samples with E_K of 0). The presence of K^+ in solution is most likely due to the incomplete exchange of NH_4^+ for naturally occurring K^+ during the NH_4^+-exchange procedure due to the higher selectivity for K^+ on Cp extraframework sites.

Phosphorous

Solution P concentrations as a function of Cp/Ap ratio and E_K are shown in Fig. 1. For a given Cp/Ap ratio, P concentrations are greater for samples with a lower E_K. This relationship reflects the higher selectivity for K^+ relative to NH_4^+ by Cp on extraframework sites as noted by Ames [23]. In other words, it is "easier" for Ca^{2+} to replace NH_4^+ on extraframework sites in the Cp than it is for Ca^{2+} to replace K^+. This increased facility to exchange extraframework NH_4^+ with Ca^{2+} results in greater synthetic Ap dissolution and higher P concentrations with

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decreasing E_K. A similar trend was observed by Allen et al. [5]. For a given E_K (1, 0.5 or 0) P concentrations initially increased with increasing Cp/Ap ratio until the solution P reached a maximum value and then decreased with increasing Cp/Ap ratio.

Phosphorous concentrations reported by Lai and Eberl [9], Chesworth et al. [10], Barbarick et al. [11] and Allen et al. [5] are shown in Figure 1 for comparison with P concentrations in solutions contacted with varying amounts of Cp and synthetic Ap. Lai and Eberl [9] combined 1 g of NH_4^+-exchanged Cp rich tuff (from Barstow, California) with 200 mg of phosphate rock (mainly carbonate apatite, from Florida) in 50 mL distilled H_2O. Chesworth et al. [10] combined 1 g apatite with 1 g unsaturated Cp in 100 mL distilled H_2O. Barbarick et al. [11] combined NH_4^+-exchanged Cp (from the Washakie Basin in Wyoming [24]) and North Carolina Phosphate Rock (NCPR) with Cp to NCPR ratios of 1.5, 3, 4.5, 6, and 7 utilizing a 2 mL/g deionized water to soil ratio. Allen et al. [5] performed experiments utilizing K^+-exchanged Cp (from San Miguel, Texas) and NCPR with Cp to NCPR ratios of 1, 2, 3, 5, 10, and 20 utilizing deionized water to soil ratios ranging from 20 to 38.1 mL/g. Data from all four studies are, for the most part, comparable with the data reported here. The reported solution P concentrations from Barbarick et al. [11] utilizing NH_4^+-exchanged Cp are identical to the $E_K = 0.5$ data reported here but are lower than the NH_4^+-exchanged Cp data ($E_K = 0$). The only significant difference between the Allen et al. [5] data and this study occur at higher Cp/Ap ratio where the P concentrations reported by Allen et al. [5] (for Cp/Ap ratios of 10 and 20) are

lower than comparable concentrations from this study (for Cp/Ap ratios of 8, 16, and 32).

The results of this study reinforce the effect of Cp/Ap ratio on P concentrations previously described by Lai and Eberl [9], Chesworth et al. [10], Barbarick et al. [11], and Allen et al. [5]. Minor differences between the data may be attributable to the different materials used in each study and/or the different fluid to solid ratios. The trend observed in this study of decreasing P concentrations at higher Cp/Ap ratio was not observed in the data from Barbarick et al. [11] and Allen et al. [5] because their experiments did not include treatments in the Cp/Ap ratio region where the trend is most apparent (i.e. higher Cp/Ap ratio data). Barbarick et al. [11] fit a linear relationship between P concentrations and Cp/Ap ratio:

$[P] = (Cp/Ap \text{ ratio}) + 0.74$ [11].

However, the data from both Barbarick et al. [11] and Allen et al. [5] do show a decrease in slope (i.e. $\Delta[P]/\Delta(Cp/Ap)$) at their highest Cp/Ap ratio, consistent with the trend observed in this study. The trend of decreasing P concentrations at higher Cp/Ap ratio in our study may be related to the amount of Ap available for dissolution.

Figure 2 shows P concentrations normalized to the minimum amount of Ap for each series of experiments (0.0758 g for this study, 2.94 g for Barbarick et al. [11], and 0.0125 for Allen et al. [5]) versus Cp/Ap ratio. The normalized P concentrations all increase linearly with Cp/Ap ratio. As the Cp/Ap ratio increases

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the number of Cp extraframework sites per g of synthetic Ap also increases. The increase in Cp extraframework sites results in an increase in the number of Ca^{2+} ions that replace NH_4^+ or K^+ per g of synthetic Ap. The increased cation exchange results in increased synthetic Ap dissolution and higher P concentrations per g of synthetic Ap with increasing Cp/Ap ratio. The observed trend in Figure 2 is consistent with the trend in the un-normalized data (Fig. 1). The NH_4^+-exchanged Cp of Barbarick et al. [11] is more efficient in dissolving naturally occurring Ap than the K^+-exchanged Cp used by Allen et al. [5]. The data from this study also indicate that NH_4^+-exchanged Cp is more efficient in dissolving synthetic Ap than the K^+-exchanged Cp, due to the higher selectivity for K^+ relative to NH_4^+ by Cp on extraframework sites, as described above.

General differences in normalized P concentrations between treatments containing naturally occurring Ap and synthetic Ap occur for both K^+-exchanged Cp and NH_4^+-exchanged Cp and may reflect on the relative solubilities of the naturally occurring Ap and synthetic Ap. The normalized P concentrations for treatments containing naturally occurring Ap and K^+-exchanged Cp [5] are greater than those for treatments containing synthetic Ap and K^+-exchanged Cp ($E_K = 1$ from this study). A comparison of treatments containing NH_4^+-exchanged Cp [11] versus $E_K = 0$ from this study) indicate the same relationship, suggesting that the naturally occurring Ap is more soluble than the synthetic Ap used in this study. Phosphorous concentrations from treatments containing Ap only (see Figure 1) also indicate that naturally occurring Ap is more soluble than the synthetic Ap. Lai and Eberl [9]

reported a P concentration of 0.55 mg/L for a treatment containing phosphate rock only in comparison to a P concentration of 0.26 mg/L for a treatment from this study containing synthetic Ap only. However, these general trends are ignoring differences in the CEC of the Cp used in each study (199 $cmol_c$ kg^{-1} for this study, 140 $cmol_c$ kg^{-1} for Barbarick et al. [11], and 170 cmolc kg^{-1} for Allen et al. [5]) as well as differences in fluid to solid ratios (40 mL/g for this study, 2 mL/g for Barbarick et al. [11], and 20 to 38.1 mL/g for Allen et al. [5]).

Calcium

Solution Ca concentrations as a function of Cp/Ap ratio and E_K are shown in Fig. 3. Solution Ca concentrations are low (ranging from 0.47 to 3.40 mg L^{-1}) in mixtures containing Cp compared to Ca in solution of the synthetic Ap only sample (19.73 mg L^{-1}). This is due to Ca, which is released by hydroxyapatite dissolution, being exchanged onto extraframework sites in the Cp. Calcium concentrations decreased with increasing Cp/Ap ratio for lower Cp/Ap ratio values (e.g. 1, 2 or 4) and are relatively constant for Cp/Ap ratio values of 8, 16, and 32. For a Cp/Ap ratio of 1, Ca concentrations increased with greater E_K. A trend between Ca concentrations and E_K was not observed in treatments with other Cp/Ap ratios. Calcium concentrations from NCPR samples reported by Allen et al. [5], ranging from 0.1 to 0.6 mg L^{-1} (Fig. 3), show a similar trend and are lower than the Ca concentrations reported here.

The lower solution Ca concentrations in treatments containing the naturally occurring NCPR [5] compared to treatments containing synthetic Ap (this study) could be attributable to differences in the solubilities of NCPR versus synthetic Ap or to differences in the CEC of the Cp in either treatment. However, the lower solution Ca concentrations in treatments containing the naturally occurring NCPR would be consistent with the NCPR being less soluble than the synthetic Ap, which is opposite the trend observed in the P data. The lower solution Ca concentrations are also inconsistent with an explanation based on differences in the CEC of the Cp. Allen et al. [5] report the CEC for the Cp used in their experiments is 170 cmolc kg^{-1} which is lower than the CEC for the Cp used in this study (199 $cmol_c$ kg^{-1}).

Magnesium

Solution Mg concentrations as a function of Cp/Ap ratio and E_K are shown in Fig. 4 and are similar in many respects to solution Ca. Measured Mg concentrations are low (ranging from 0.11 to 6.68 mg L^{-1}) compared to the synthetic Ap only sample, which had a solution Mg concentration of 36.21 mg L^{-1}. For a given Cp/Ap ratio, Mg concentrations are greater for samples with a greater E_K. This relationship is more pronounced at lower Cp/Ap ratio values (e.g. 1, 2, or 4) and does not exist at Cp/Ap ratio values of 16 or 32. Like P, the relationship between Mg concentration and E_K may be due to the higher ion selectivity for K^+ over NH_4^+ on extraframework sites of Cp. Magnesium does not compete very well with K^+ on extraframework sites but does slightly better with NH_4^+.

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Potassium

Solution K concentrations as a function of Cp/Ap ratio and E_K are shown in Fig. 5.

For both an E_K of 1.0 and 0.5 there is a decrease in K concentration with increasing

Cp/Ap ratio reflecting that the release of K^+ from Cp extraframework sites is driven

by cation exchange with Ca^{2+} that is released by the dissolution of the synthetic Ap.

The concentration of K as well as the decrease in K concentration with increasing

Cp/Ap ratio (e.g. slope of the [K] vs. Cp/Ap ratio line in Fig. 5) is greater for $E_K = 1$

in comparison to $E_K = 0.5$ reflecting that K is the only exchangeable cation present

on extraframework sites of the Cp for the $E_K = 1$ samples. Potassium

concentrations from K-exchanged Cp and NCPR samples reported by Allen et al.

[5] are shown in Figure 5 and for a given Cp/Ap ratio are lower than the K

concentrations for the $E_K=1$ samples reported here.

Ammonium

Solution NH_4^+ concentrations as a function of Cp/Ap ratio and E_K are shown in

Fig. 6 and show trends similar to K. The concentration of NH_4^+ as well as the

decrease in NH_4^+ concentration with increasing Cp/Ap ratio (e.g. slope of the $[NH_4^+]$

vs. Cp/Ap ratio line in Fig. 6) is greater for $E_K = 0$ in comparison to $E_K = 0.5$

reflecting that NH_4^+ is the dominant exchangeable cation present on Cp

extraframework sites for the $E_K = 0$ samples.

Inferences on Nutrient Availability

Schofield [25] addresses nutrient availability in soils by distinguishing between nutrient intensity (i.e. represented by the concentration of the soil solution) and nutrient quantity or capacity (i.e. the amount of potentially available nutrient in the soil). The results of this study can be used to assess only the initial nutrient intensity. Kinetic studies, plant growth studies, and/or special soil tests are required to address nutrient quantity.

The range of P concentrations in solution observed in this study (0.57 to 14.99 mg L^{-1}) is greater than soil solution concentrations of 0.19 to 0.31 mg L^{-1} reported by Tisdale et al. [26] and the 0.003 to 0.3 mg L^{-1} reported by Havlin et al. [27] to be adequate for a variety of crops in the field. The P in solution from Cp plus synthetic Ap substrates are also greater than the 0.14 mg L^{-1} annual average soil solution P concentration reported by Marschner [28] and Mengel et al. [29] for arable soils. The P concentrations in solution observed in this study, however, are lower than Bugbee and Salisbury's [30] estimated ideal P concentration in a hydroponic solution (31 mg/kg water) for environmentally controlled plant growth chambers (e.g. hydroponic system at a Lunar outpost).

Calcium concentrations in solution range from 0.47 to 3.40 mg L^{-1}. These values are low compared to Lindsay's ([31] Table 1.1) selected average soil solution concentration of 339.5 mg L^{-1} (adjusted to a fluid:solid ratio of 40) and to the concentration of a Hoagland's nutrient solution (approximately 200 mg L^{-1}, [32] or to the half-strength Hoagland's nutrient solution used as a control in NASA's

zeoponic plant growth experiments [16, 33-34]. The Ca concentrations reported here are also low compared to the minimum required for good corn yields (14.8 mg L^{-1}) or to the range of 8.02 to 44.9 mg L^{-1} for a typical soil solution, both reported by Tisdale et al. [26]. They are also less than the 66.1 mg L^{-1} annual average soil solution Ca concentration reported by Marschner [28] and Mengel et al. [29] for arable soils. The Ca concentrations in solution observed in this study are lower than Bugbee and Salisbury's [30] estimated ideal Ca concentration of 50 mg kg-water^{-1} for a hydroponic system at a Lunar outpost. The Ca concentrations in solution measured in this study are within the "just adequate" range of 0.24 to 40 mg L^{-1} reported by Jones [35] in his guide to hydroponic plant growth systems.

Magnesium concentrations in solution observed in this study (0.11 to 6.68mg L^{-1}) are less than the 11.9 mg L^{-1} average reported by Marschner [28] and Mengel et al. [29] for arable soils. They are also low when compared to the ideal concentration (16 mg kg-water^{-1}) for Mg in a hydroponic solution for environmentally controlled plant growth chambers of Bugbee and Salisbury [30]. Except for treatments with a Cp/Ap ratio of 1 and an E_K of 1 or 0.5, Mg concentrations are low compared to typical soil solution concentrations of 5 to 50 mg L^{-1} in temperate region soils [27].

Ammonium-N concentrations range from 19.7 to 73.6 mg L^{-1}, which are far above the 0.9 mg L^{-1} annual average soil solution NH_4^+ concentration reported by Marschner [28] and Mengel et al. [29] for arable soils. However the total N concentration (i.e. NH_4^+-N and NO_3^--N) reported by Marschner [28] and Mengel et

al. [29] is 193 mg L^{-1}, far greater than the range for NH_4^+-N reported here. Bugbee and Salisbury's [30] estimated ideal total N concentration of 202 mg/kg-water^{-1} for a hydroponic system at a Lunar outpost is also greater than the range for NH_4^+-N reported here.

All of the measured K concentrations (14.8 to 104.8 mg L^{-1}) are greater than the range of 1 to 10 mg L^{-1} common to soil solutions as reported by Havlin et al. [27]. Except for the samples with E_K = 0.5 and Cp/Ap ratios of 16 or 32, the K concentrations in this study are greater than the 19.9 mg L^{-1} average reported by Marschner [28] and Mengel et al. [29] for arable soils. Tisdale et al [26] report optimum soil solution K concentrations in the range of 9 to 60 mg L^{-1}. All of the K concentrations reported here are greater than their lower value and the samples with E_K = 1 and Cp/Ap ratios of 1, 2, 4, and 8 are greater than their upper value. The K concentrations in solution observed in this study are lower than Bugbee and Salisbury's [30] estimated ideal K concentration of 156 mg kg-water^{-1} for a hydroponic system at a Lunar outpost.

CONCLUSIONS

Dissolution of synthetic Ap in the presence of Cp results in greater dissolution of the synthetic Ap because it is driven by ion exchange of Ca^{2+} onto extraframework sites in the Cp, releasing K^+ and/or NH_4^+ into solution. The specific amounts of these macronutrients in solution, as well as calcium, are a function of the Cp/Ap ratio in the sample and to the ratio of K^+ and/or NH_4^+ on the extraframework

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sites in Cp. Solution concentrations of NH_4^+, K, Ca, and Mg all decrease with increasing Cp/Ap ratio in the sample. Potassium and NH_4^+ exhibit similar trends due to the fact that both ions originate on Cp extraframework sites and undergo cationic exchange with Ca^{2+} and other ions. Calcium and Mg show similar trends due to their common origin in the synthetic Ap crystalline structure. Solution concentrations of P initially increased until a maximum value was reached and then decreased with increasing Cp/Ap ratio in the sample for these experiments. The Cp/Ap ratio at which the maximum solution concentration of P occurs varies as a function of E_K of the Cp. The observed trends in solution P concentrations as a function of Cp/Ap ratios are comparable with data reported for naturally occurring Ap in combined PR and Cp systems [5, 9-11]. The macronutrients P, NH_4^+-N, and K are available to plants at sufficient levels. Magnesium concentrations are marginal. Concentrations of Ca^{2+} in solution may be insufficient for plant growth. Calcium is exchanged onto the extraframework sites of Cp, which reduces its concentration in solution. Plant growth experiments on wheat grown in zeoponic substrates have resulted in excessive sterile tillers and poor seed production that has been attributed to a Ca deficiency in the soil solution [16, 34]. This Ca deficiency might be remedied by: 1) development of a procedure to reduce the Ca ion exchange by the Cp or 2) addition of a second Ca-bearing, soluble, mineral such as calcite, dolomite or wollastonite (e.g. see Beiersdorfer et al. and Gruener et al., this volume).

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Table 1. Composition of clinoptilolite (Cp) and hydroxyapatite (Ap) used in experiments.

Cp		Ap	
oxide	wt. %	oxide	wt. %
SiO_2	70.36	CaO	46.8
Al_2O_3	13.99	P_2O_5	39.61
Na_2O	4.39	Fe_2O_3	1.21
K_2O	1.64	MgO	2.25
CaO	1.42	SiO_2	0.59
MgO	0.18	SO_3	2.07
FeO	0.1	OH	3.61
MnO	0.01		
TiO_2	0.02		
Cr_2O_3	0.01		
P_2O_5	0.01		
SO_2	0.02		

element	mg/L	element	mg/L
Ni	<18.5		
Co	0.8	Na	23.74
Sr	421	K	18.26
Cs	2	Mn	330
Rb	81.6	Cu	28.9
Zr	206.3	Zn	282
Ba	906	Sr	140
As	1.6		

Table 2: Solution pH, ionic strength (I.S.), and concentrations of P, K, NH_4, Mg and Ca as a function of Cp/Ap ratio and E_K.
Values represent average of three replicates. Numbers in parentheses represent one standard deviation. n.a. = not analyzed

Cp /Ap	E_K	pH		I.S. (mmol/L)		P (mg/L)		NH4 (mg/L)		K (mg/L)		Mg (mg/L)		Ca (mg/L)	
0	n.a.	7.70	(0.11)	4.03	(0.20)	0.26	(0.12)	n.a.		n.a.		36.21	(2.43)	19.73	(0.32)
1	1	7.87	(0.20)	3.78	(0.06)	0.57	(0.03)	n.a.		104.85	(0.73)	6.68	(0.33)	3.40	(0.09)
2	1	7.90	(0.02)	3.46	(0.33)	0.98	(0.01)	n.a.		98.75	(1.54)	3.01	(0.13)	1.88	(0.04)
4	1	7.89	(0.06)	2.80	(0.08)	1.77	(0.03)	n.a.		86.59	(1.78)	1.38	(0.11)	1.10	(0.12)
8	1	7.94	(0.05)	2.35	(0.17)	3.10	(0.24)	n.a.		70.43	(3.15)	0.58	(0.16)	0.79	(0.05)
16	1	7.87	(0.15)	1.87	(0.08)	4.06	(0.41)	n.a.		58.93	(4.72)	0.28	(0.06)	0.88	(0.44)
32	1	7.88	(0.10)	1.49	(0.03)	4.59	(0.68)	n.a.		47.60	(2.16)	0.14	(0.01)	0.49	(0.03)
1	0.5	8.22	(0.01)	5.07	(0.03)	1.00	(0.05)	45.17	(0.31)	33.48	(0.46)	5.26	(0.26)	3.07	(0.31)
2	0.5	8.29	(0.01)	4.45	(0.03)	2.01	(0.08)	43.16	(0.10)	30.35	(0.34)	2.26	(0.10)	2.05	(0.33)
4	0.5	8.31	(0.01)	3.80	(0.03)	4.50	(0.28)	39.21	(0.48)	27.24	(0.52)	1.05	(0.03)	1.20	(0.13)
8	0.5	8.20	(0.02)	3.01	(0.16)	6.94	(0.79)	32.16	(1.75)	21.93	(1.01)	0.44	(0.07)	1.06	(0.21)
16	0.5	8.09	(0.05)	2.41	(0.11)	8.53	(0.68)	26.01	(1.42)	17.59	(0.68)	0.21	(0.03)	0.80	(0.15)
32	0.5	8.03	(0.03)	1.85	(0.09)	7.91	(0.30)	19.73	(1.07)	14.83	(0.64)	0.12	(0.02)	0.90	(0.19)
1	0	8.35	(0.01)	5.69	(0.04)	2.43	(0.15)	73.64	(0.51)	1.21	(0.02)	2.48	(0.02)	2.12	(0.01)
2	0	8.39	(0.02)	4.95	(0.08)	4.95	(0.10)	68.06	(0.57)	1.06	(0.09)	1.02	(0.04)	1.23	(0.39)
4	0	8.36	(0.02)	4.20	(0.15)	9.39	(0.50)	59.11	(2.39)	0.94	(0.07)	0.44	(0.05)	0.92	(0.11)
8	0	8.28	(0.02)	3.66	(0.12)	14.19	(1.17)	51.57	(1.46)	0.82	(0.08)	0.22	(0.02)	0.47	(0.05)
16	0	8.15	(0.01)	2.73	(0.07)	12.83	(0.62)	37.88	(1.09)	0.68	(0.03)	0.11	(0.01)	0.62	(0.17)
32	0	7.94	(0.02)	1.92	(0.06)	11.02	(0.90)	26.32	(1.23)	0.63	(0.23)	0.17	(0.17)	0.84	(0.60)

Figure 1: Solution P concentration as a function of Cp to Ap Mass Ratio and E_K. Solid symbols represent the average of three replicates. Error bars represent ± 1 σ. Data from Lai and Eberl [9], Chessworth et al. [10] and Barbarick et al. [11] have $E_K = 0$. Data from Allen et al. [5] have $E_K = 1$. Lines connecting data points are added to show trends only and do not imply curve fitting.

Figure 2: Normalized solution P concentration as a function of Cp to Ap Mass Ratio and E_K. Solid symbols represent the average of three replicates. Data from Barbarick et al. [11] have $E_K = 0$. Data from Allen et al. [5] have $E_K = 1$. Lines represent linear fit of data by least squares regression.

Fig. 3: Solution Ca concentration as a function of Cp to Ap Mass Ratio and E_K. Solid symbols represent the average of three replicates. Error bars represent ± 1 σ. Data from Allen et al. [5] have $E_K = 1$. Lines connecting data points are added to show trends only and do not imply curve fitting.

Fig. 4: Solution Mg Concentration as a function of Cp to Ap Mass Ratio and E_K. Symbols represent the average of three replicates. Error bars represent ± 1

σ. Lines connecting data points are added to show trends only and do not imply curve fitting.

Fig. 5: Solution K Concentration as a function of Cp to Ap Mass Ratio and E_K. Solid symbols represent the average of three replicates. Error bars represent ± 1 σ. Data from Allen et al. [5] have $E_K = 1$. Lines connecting data points are added to show trends only and do not imply curve fitting.

Fig. 6: Solution NH_4 Concentration as a function of Cp to Ap Mass Ratio and E_K. Symbols represent the average of three replicates. Error bars represent ± 1 σ. Lines connecting data points are added to show trends only and do not imply curve-fitting.

FIG 2

FIG 3

FIG 4

FIG6